

Optimization of H₂S and NH₃ Absorption Condition to Minimize CO₂ Absorption in a Water-Wash Process

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ABSTRACT

The purification of coke oven gas (COG) is necessary with respect to the environmental protection. Among the components to be removed from coke oven gas are NH₃ and H₂S. NH₃ and H₂S are required to be removed because they are the source of NO_x and SO_x emission in the stack gas. For the purpose of the best removal of these impurities the operation of the facilities should be optimized accordingly with the limitations imposed.

In order to optimize H₂S and NH₃ absorption condition against the interference of CO₂, theoretical and experimental studies were carried out. First of all the mass transfer coefficients, phase equilibrium constants, and chemical equilibrium constants for the three compounds were derived from theoretical study. Since the CO₂ dissociation reaction is relatively slow, the free CO₂ that gives rise to vapor pressure was estimated basically from chemical reaction rate. The dissociation reaction rates of H₂S and NH₃ were, however, known to be so fast that the equilibrium state is assumed. The free H₂S and NH₃, therefore, were calculated from the equilibrium concentrations. Numerical simulations for the scrubbers were carried out with the models from the derivation of the previous and present works. The calculation results were compared with the data from the real process and the best models were selected. Some modifications were also made for the best fitting and the optimum operation conditions for the absorption towers were found by using the simulation program.

Temperature control is critical as the undesirable CO₂ absorption increases rapidly with the temperature rise. When temperature increases from 20 to 30 °C, CO₂ absorption is almost doubled. Absorbing liquid flow rate was found to be one of the important factor to control the absorption efficiencies of H₂S, NH₃, and CO₂ when temperature limitation is imposed. The other important factor is NH₃ concentration in the concentrated ammonia liquor which is used for H₂S absorption. Increasing NH₃ concentration is effective on H₂S absorption up to 10g/L but further addition of NH₃ only increases CO₂ absorption.

1. Introduction

Major changes that have occurred in coke oven gas (COG) treatment during the recent

decades were due either to economic conditions or to the environmental restrictions. Another factor becoming more and more prevalent is the increased concern for the health and safety of coke plant workers. The COG has lost its value as a source of raw material for the organic chemical industry. Petroleum and natural gas have taken this over. The only asset of the gas left is its heating value of approximately 17500kJ/Nm^3 . Consequently the aim of COG treatment today is to produce an environmentally acceptable fuel gas at minimum cost. Mainly to lower the SO_x emission in the stack gas, H_2S should be removed. Ammonia is removed down to a residual concentration because of its corrosiveness toward the gas lines and being a source of NO_x emission.

In the coke oven gas (COG) purification technology, the use of ammoniacal solutions for H_2S removal is a very old approach. It has always been appealing because it employs only the chemicals that are generated in the plant itself. It was not widely used for many years because of poor H_2S removal, high ammonia losses with the H_2S product, and extensive corrosion. Recently many improvements to this basic process have been developed and it is used in many plants today.

In most processes employing ammonia, the ammonia is scrubbed from gas in an absorber using treated water or condensate, and the effluent ammonia washwater is introduced into the top of the H_2S scrubber, which precedes the ammonia absorber in the gas stream. The foul liquor from the bottom of the H_2S scrubber is pumped to a deacidifier, where mainly the H_2S and the total ammonia production leaves the system in a vapor state, which is called acid gas, for further treatment such as oxidation in a Claus Plant. The bottom liquor from the deacidifier is ammonia rich and is recycled to the H_2S scrubber at point somewhat below the top. An ammonia still is provided to strip the excess flushing liquor, and this ammonia vapor is piped to the deacidifier so that this ammonia can be used to elevate the ammonia concentration in the bottom liquor from the deacidifier. Fig. 1 shows the typical diagram of this process.

Because CO_2 content in the coke oven gas is very high, the absorption of CO_2 is one of the obstacles of this process especially when it is in a state of high temperature. The increase of CO_2 absorption will cause the decreased H_2S absorption and the lower efficiencies in the distillation and sulfur recovery processes. The absorption rate of CO_2 increases with the increase of temperature [1, 8b] and total amount of CO_2 absorbed increases with the increased contact time between liquid and gas when both CO_2 and H_2S are present [2]. This research is focused on minimizing CO_2 absorption and maximizing H_2S and ammonia absorption.

2. Mathematical modelling

The two-film theory model which can be summarized in one equation such as Eq. (1) was used for the calculation [3].

$$-Vdy = K_y a (y - y^*) S dZ \quad (1)$$

$$r = k_x (x_i - x)$$

$$r = k_y (y - y_i)$$

$$r = K_y (y - y^*)$$

$$\frac{1}{K_y} = \frac{1}{k_y} + \frac{m}{k_x}$$

r : Mass transfer rate

y : Mole fraction of solute in bulk gas

y_i : Mole fraction of solute in gas at interface

x : Mole fraction of solute in liquid in bulk liquid

x_i : Mole fraction of solute in liquid at interface

y^* : Composition of the vapor that would be in equilibrium with the
bulk liquid of composition x

k_x : Individual mass transfer coefficient in liquid phase, based on mole fraction differences

k_y : Individual mass transfer coefficient in gas phase, based on mole fraction differences

K_y : Overall mass transfer coefficient in gas phase

m : Slope of equilibrium curve

S : Cross sectional area of the packed tower

V : Molar flow rate

a : Area of interface per unit packed volume

Fig. 2 shows concentration gradient in case of absorption that gives basis for the two-film theory. Film is defined as the region in which there is an abrupt change in concentration and this region is considered to cause almost all resistance to mass transfer. In the sense of overall mass transfer coefficient K_y , a driving force for the absorption exists because the concentration in gas is higher than the equilibrium concentration .

The term $1/K_y$ can be considered an overall resistance to mass transfer, and the terms m/k_x and $1/k_x$ are the resistances in the liquid and gas films. The gas film mass transfer coefficient k_y is derived from the Colburn analogy and expressed like a following equation.

$$\frac{k_c}{u_0} N_{Sc}^{2/3} = 1.17 N_{Re}^{-0.415} \quad (2)$$

The Reynolds number used in this equation can be calculated from the gas flow rate, the size of packing, the porosity, and the viscosity fo the gas. Schmidt number is calculated from Eq. (3).

$$N_{Sc} = \frac{\mathbf{m}}{\mathbf{r} D_{AB}} \quad (3)$$

\mathbf{m} : Viscosity of COG

\mathbf{r} : Density of COG

D_{AB} : Diffusivity

Here, the diffusivity is calculated from the theory that is recommended for mixtures of nonpolar gases or of a polar with a nonpolar gas and expressed like Eq. (4) because no dependable diffusivity data of gas impurities in the COG could be obtained [4a].

$$D_{AB} = \frac{10^{-4} (1.084 - 0.249 \sqrt{1/M_A + 1/M_B}) T^{3/2} \sqrt{1/M_A + 1/M_B}}{P_t (r_{AB})^2 f(kT/\mathbf{e}_{AB})} \quad (4)$$

D_{AB} : Diffusivity (m²/s)

T : Absolute temperature (K)

M_A, M_B : Molecular weight of A and B

P_t : Absolute pressure (N/m²)

r_{AB} : Molecular separation at collision (nm = $(r_A + r_B)/2$)

\mathbf{e}_{AB} : Energy of molecular attraction ($\sqrt{\mathbf{e}_A \mathbf{e}_B}$)

k : Boltzmann's constant

Here, $f(kT/e)$ can be correlated with kT/e like following equation referring to collision

function graph [4a]:
$$f\left(\frac{kT}{e}\right) = 1.04175 - 0.3885\left(\frac{kT}{e}\right) + 0.065\left(\frac{kT}{e}\right)^2.$$

The k_c that is calculated by Eq. (4) is converted to k_y .

The mass transfer coefficient in liquid is calculated by the penetration theory represented as Eq. (5).

$$k_c = 1.13 \sqrt{\frac{D_L}{t_T}} \quad (5)$$

Here, t_T is average reaction time in liquid film because NH_3 , H_2S , and CO_2 react each other and the reactions are so rapid that the diffusion phenomena can not affect the concentration gradient in the liquid film [8a].

Diffusivities of the gas components in water are calculated from the equations based on Wilke and Chang's theory [4b, 5]. The derived diffusivities for NH_3 , H_2S , and CO_2 in water are as follows:

$$D_{\text{LNH}_3} = \frac{7.013 \times 10^{-15} T}{m} \quad (6)$$

$$D_{\text{LCO}_2} = \frac{6.248 \times 10^{-15} T}{m} \quad (7)$$

$$D_{\text{LH}_2\text{S}} = \frac{5.133 \times 10^{-15} T}{m} \quad (8)$$

The k_c that is calculated by Eq. (5) is converted to k_x .

Area of interface per unit packed volume is calculated by a following equation correlated for the Raschig ring packing [4c] because no correlation for the expanded metal packing was found.

$$a = 40.11(808G_y^n / r_G^{0.5})^{0.11Gx-0.022} G_x^{0.14} \quad (9)$$

G_y : Superficial gas mass velocity

G_x : Superficial liquid mass velocity

Equilibrium concentration in gas phase was calculated from free NH_3 , H_2S , and CO_2 concentrations in water that give rise to vapor pressure. Free NH_3 , H_2S , and CO_2 concentrations remaining after chemical reaction can be calculated from chemical equilibrium and the equilibrium constants were derived from thermodynamic data and Stumm and Morgan [6]. Equilibrium vapor pressures in gas phase for NH_3 , H_2S are also calculated from the correlations of Van Krevelen et al. [7]. Vapor pressure for CO_2 is calculated by using the correlation for Henry's constant from Stumm and Morgan [6]. The free CO_2 concentration, however, is not usually determined by the chemical equilibrium because reaction rate of dissociation is too low for the equilibrium to be reached. The following reaction rate equation is, therefore, used basically to calculate free CO_2 concentration.

$$-\frac{d[\text{CO}_2]}{dt} = k[\text{OH}^-][\text{CO}_2] \quad (10)$$

Here, the reaction rate constant k is calculated by the following correlation [8b].

$$\log k = 13.635 - 2895/T \quad (11)$$

Eq.(1) is solved with parameters derived above, and Eq.(1) is transformed to be a differential equation.

$$\frac{dy}{dZ} = \frac{-K_y a(y - y^*)S}{V} \quad (12)$$

This equation is solved numerically by the Euler method.

$$y_{n+1} = y_n + \frac{dy}{dZ} \Delta Z \quad (13)$$

The whole tower is divided up into equidistant intervals and this interval becomes differential height ΔZ . The concentrations in the liquid and gas phase are determined step by

step which is differential height apart. Fig.3 is an example of H₂S scrubber. Because we don't know the concentrations in both effluent liquid and gas, the concentrations in either effluent liquid or gas should be assumed to enable the equations to be solved. Once the concentrations are assumed, assumed values are corrected by the iteration method.

The object process for the optimization is shown in Fig.4. This process is a real process that is under operation in POSCO and the operation data were compared with calculation results and the parameters of the models selected were corrected so that the calculation results coincide the real data.

3. Result and discussion

Firstly the relationships between ammonia concentration and H₂S and CO₂ concentrations in the ammonia rich liquor are determined through experiments. Fig.5 shows relationship between ammonia and H₂S concentration and this plot can be correlated as follows:

$$C_{hs} = 4.6 \times 10^{-3} C_{amm}^2 + 7.935 \times 10^{-3} C_{amm} \quad (14)$$

Fig.6 shows relationship between ammonia and CO₂ concentration and this plot can be correlated as follows:

$$C_{ca} = 0.02 C_{amm}^2 - 0.0484 C_{amm} \quad (15)$$

Both relationships for H₂S and CO₂ are used for the optimization of the ammonia concentration in the ammonia rich liquor.

Some operation conditions for the model calculations were fixed for the ease of calculation and comparison, and those are Coke Oven Gas flow rate 75000Nm³/h, and composition of COG before H₂S scrubber where H₂S concentration is assumed to be 5g/Nm³ and NH₃ to be 5g/Nm³ and CO₂ to be 40g/Nm³.

In order to determine the effect of the temperature on the absorption efficiency of the those three components some calculations were carried out in the following conditions: ammonia rich liquor flow rate 120m³/h, soft water 20m³/h, stripped liquor 25m³/h, the condensate liquor flow rate into ammonia scrubber #1 35m³/h, and ammonia concentration in ammonia rich liquor 13g/L. Fig.7 shows the result. When temperature increases CO₂ absorption efficiency is almost doubled and H₂S removal efficiency decreases accordingly.

Fig.8 shows the effect of ammonia concentration in the ammonia rich liquor. The

conditions are: ammonia rich liquor flow rate $110\text{m}^3/\text{h}$, stripped liquor $30\text{m}^3/\text{h}$, soft water $25\text{m}^3/\text{h}$, the condensate liquor $35\text{m}^3/\text{h}$, and the temperature 30°C . In this figure we can find out that the ammonia concentration increase is not effective for H_2S absorption if the concentration is more than about 10g/L .

Fig. 9 shows the effect of stripped liquor flow rate on the absorption efficiencies of NH_3 , H_2S , and CO_2 . The conditions for calculation are: ammonia rich liquor+stripped liquor $140\text{m}^3/\text{h}$, soft water $25\text{m}^3/\text{h}$, condensate liquor $35\text{m}^3/\text{h}$, ammonia concentration in ammonia rich liquor 10g/L , and temperature 30°C . From this figure stripped liquor flow rate from ammonia still is found to be very important factor second to the temperature.

4. Conclusion

Temperature control is critical as the undesirable CO_2 absorption increases rapidly with the temperature rise. When temperature increases from 20°C to 30°C , CO_2 absorption is almost doubled. Absorbing liquid flow rate was found to be one of the important factor to control the absorption efficiencies of H_2S , NH_3 , and CO_2 when temperature limitation is imposed. The other important factor is NH_3 concentration in the concentrated ammonia liquor which is used for H_2S absorption. Increasing NH_3 concentration is effective on H_2S absorption up to 10g/L but further addition of NH_3 only increases CO_2 absorption.

5. References

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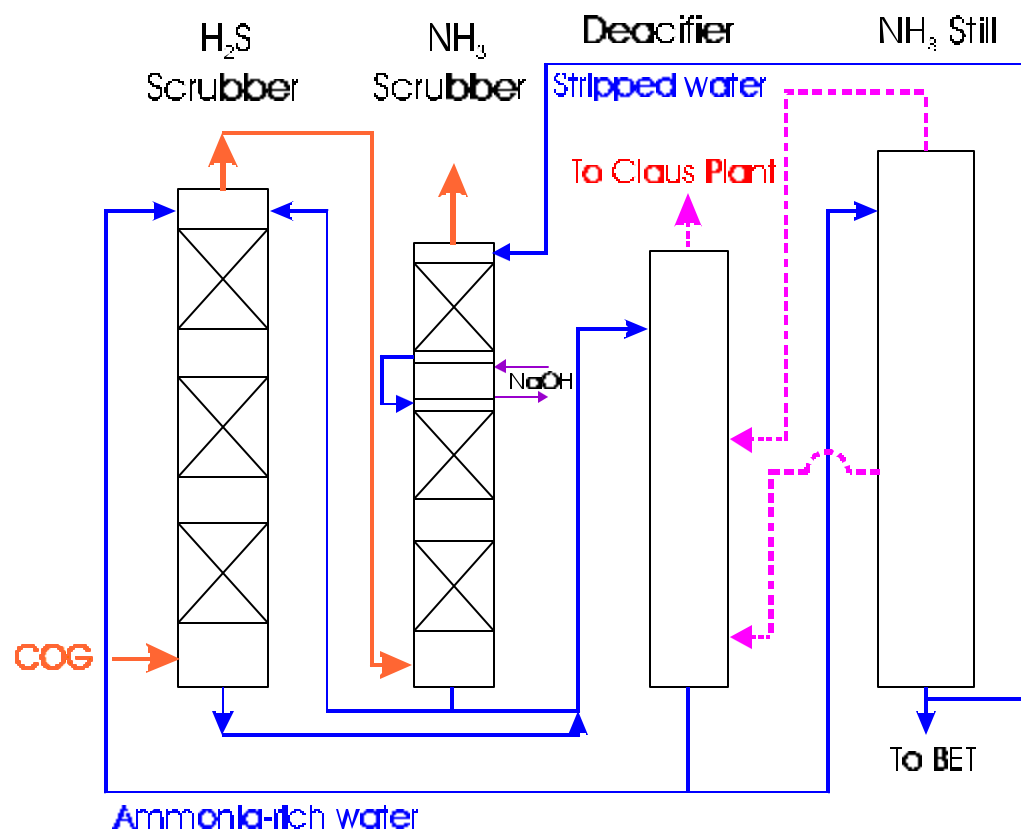


Fig. 1 Typical diagram of the Ammonia process for H₂S removal

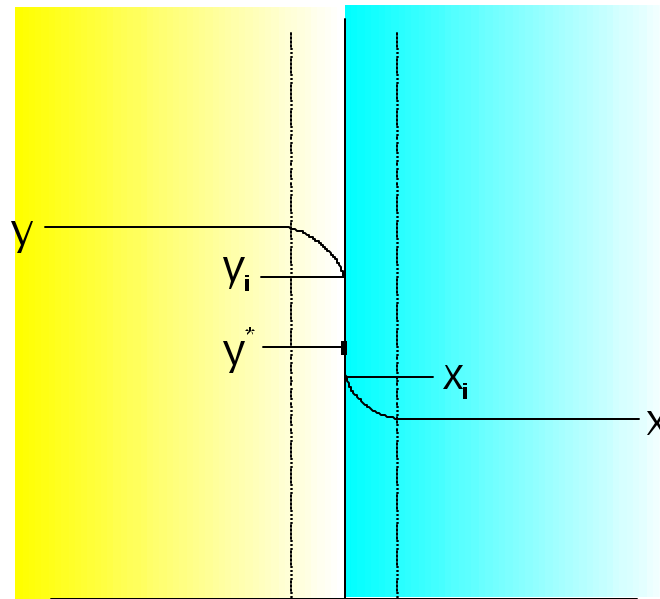


Fig. 2 Concentration gradient in case of absorption

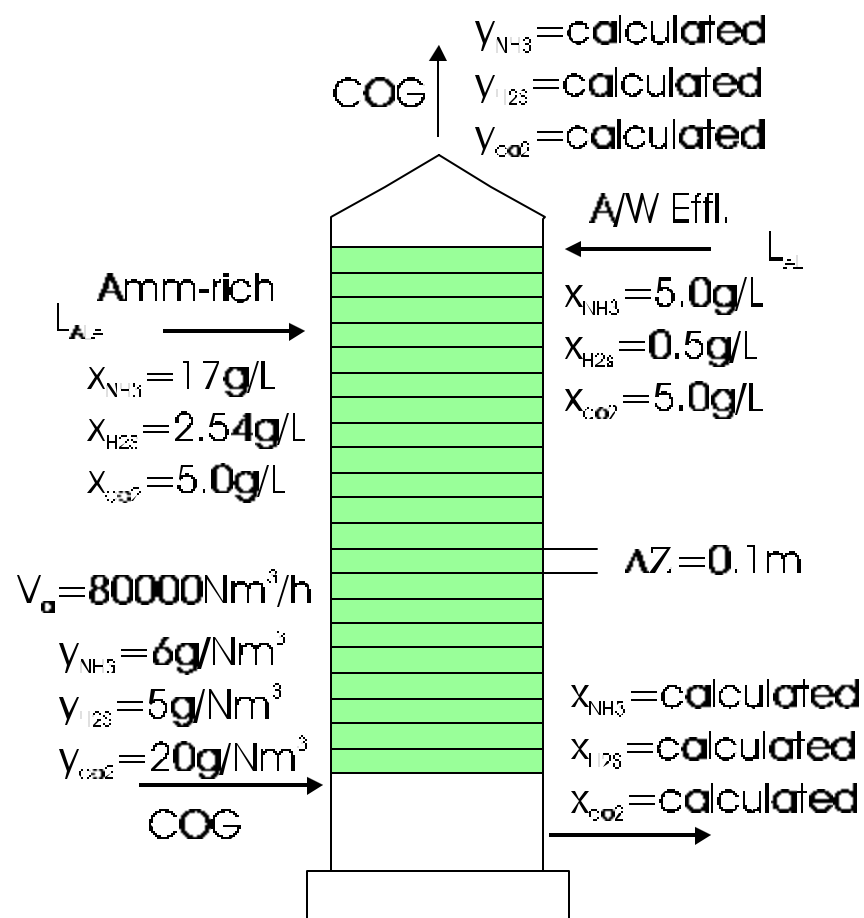


Fig. 3 Calculation example of absorption tower

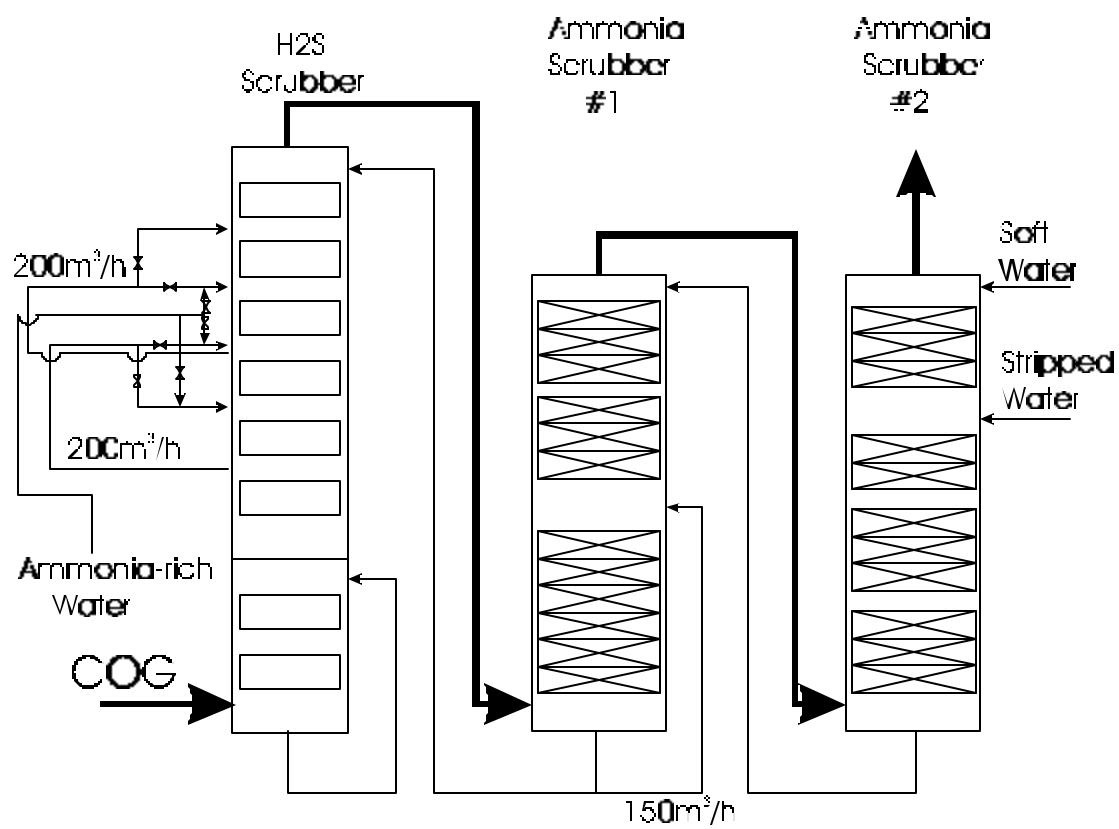


Fig. 4 The object process to be optimized

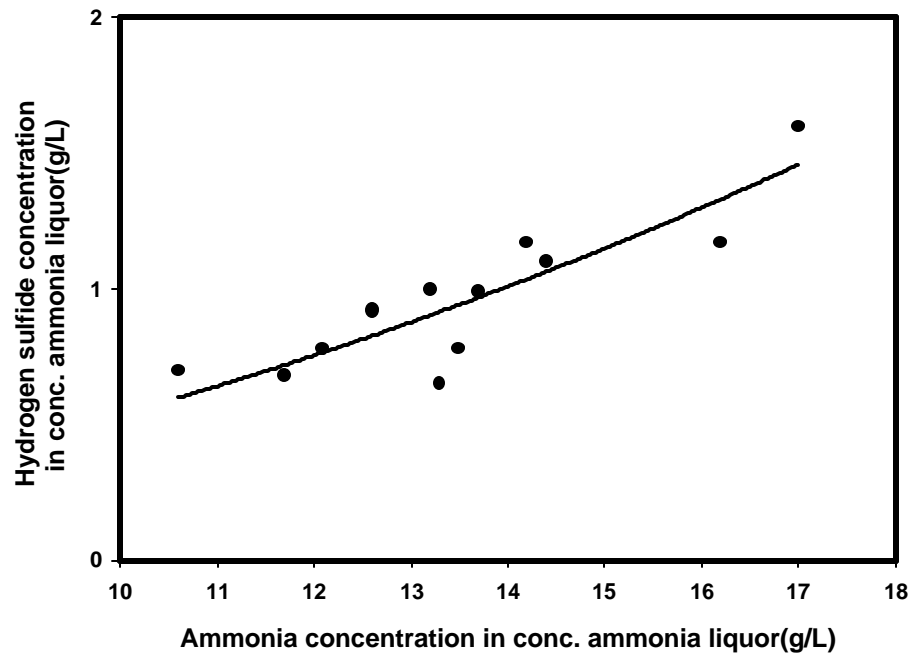


Fig. 5 Relationship between ammonia and H₂S concentration in ammonia rich liquor

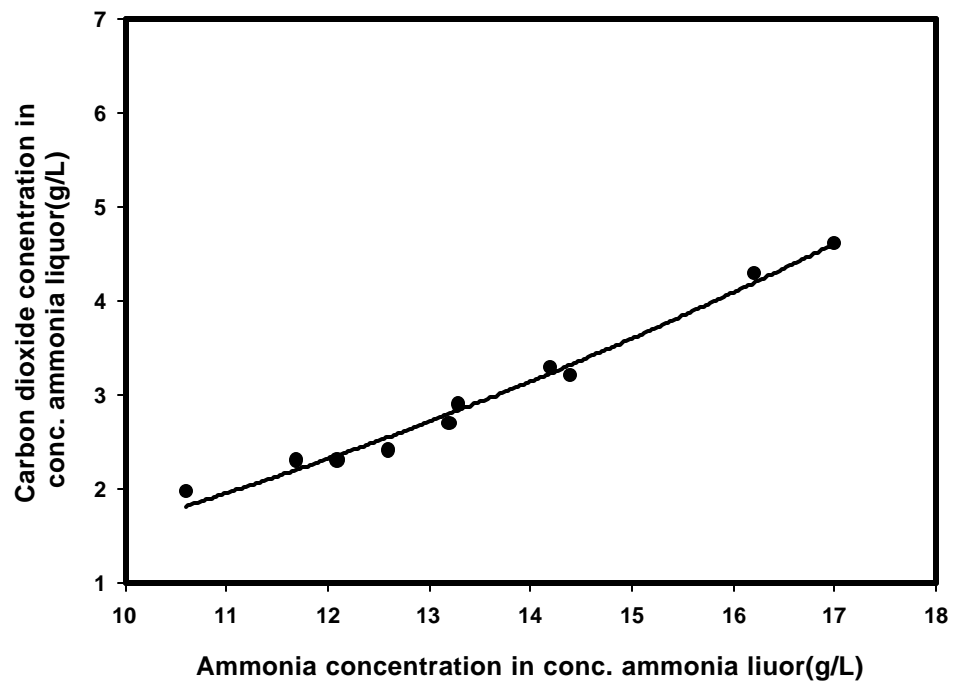


Fig. 6 Relationship between ammonia and CO₂ concentration in ammonia rich liquor

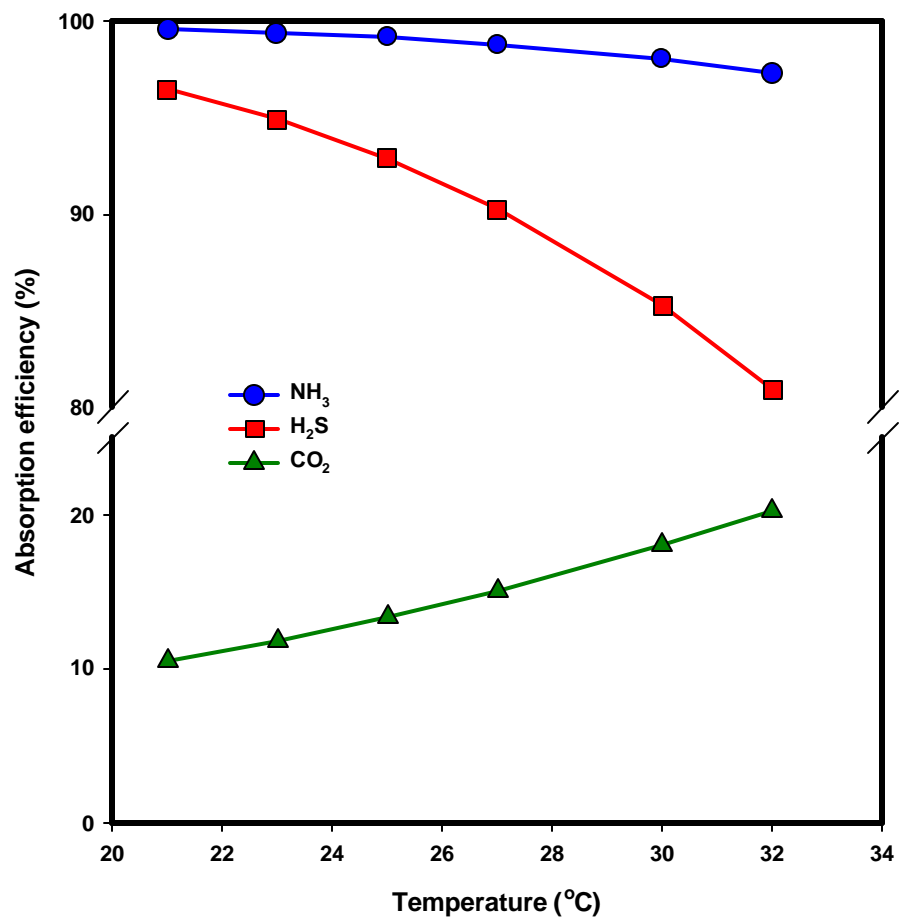


Fig. 7 Effect of temperature on the absorption efficiencies of NH_3 , H_2S , and CO_2

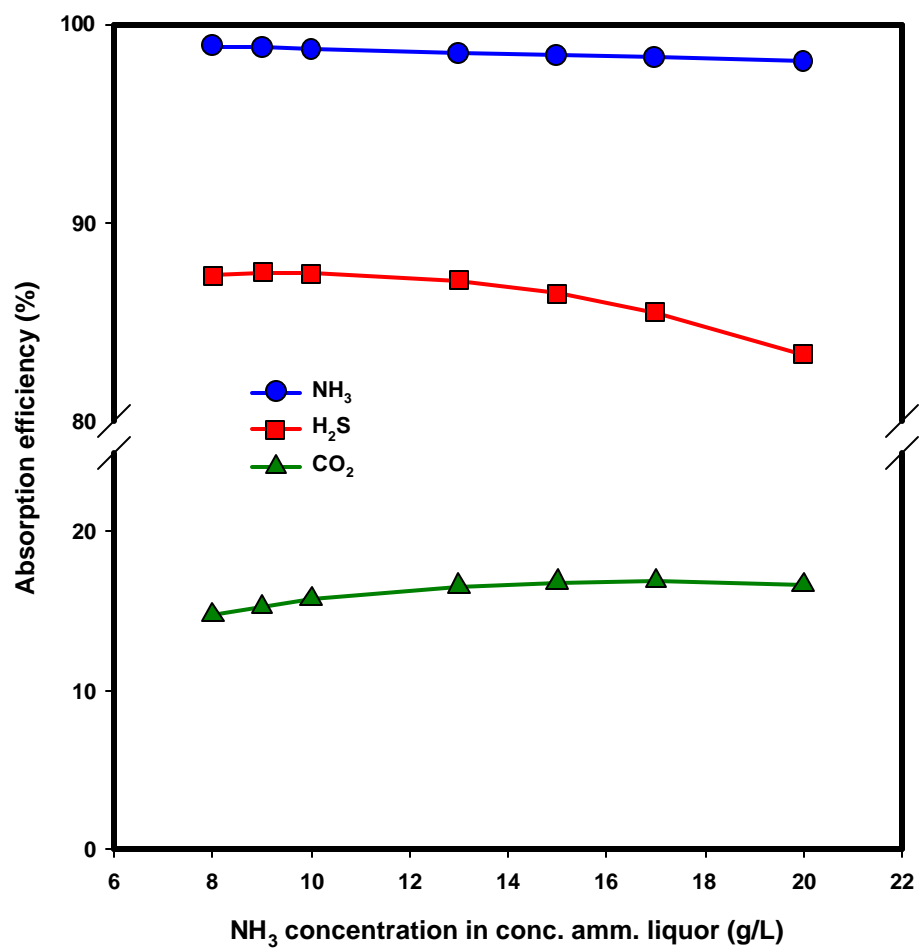


Fig. 8 Effect of ammonia concentration in ammonia rich liquor on the absorption efficiencies of NH₃, H₂S, and CO₂

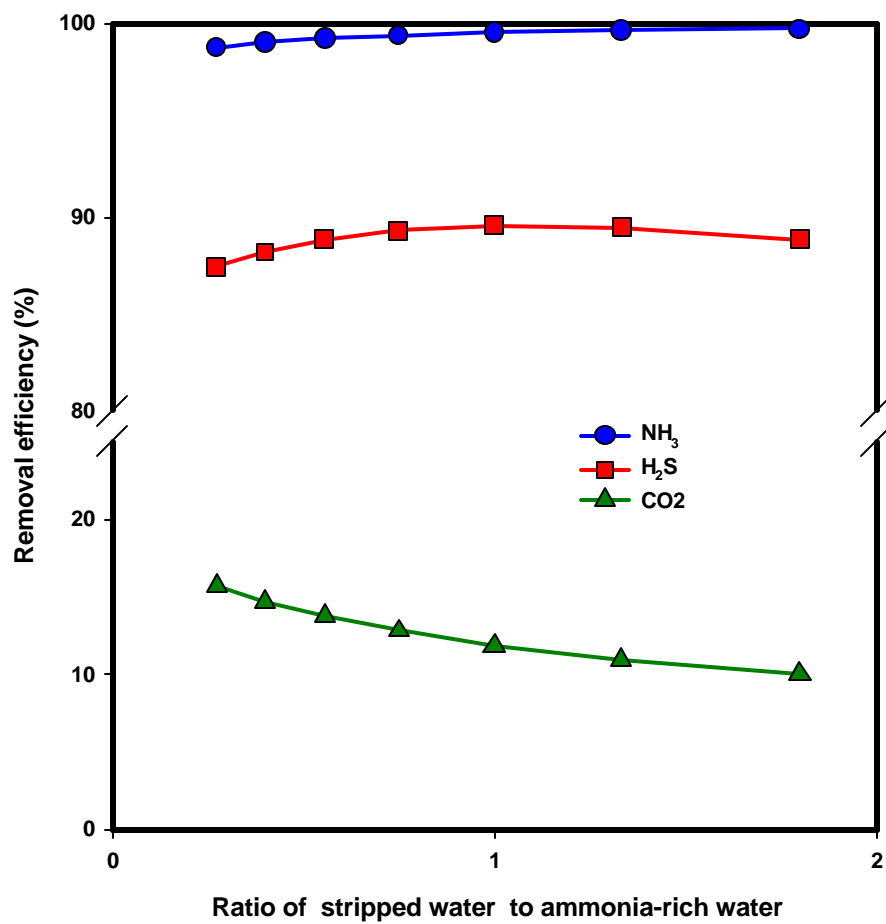


Fig. 9 Effect of stripped liquor flow rate on the absorption efficiencies of NH₃, H₂S, and CO₂